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Syngas Reactions. 6.[†] Aliphatic Alcohols and Esters from Synthesis Gas

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A series of ruthenium bimetallic catalysts, comprising a ruthenium source, such as $Ru_3(CO)_{12}$, and a second metal selected from halogen-free titanium, zirconium, cobalt, manganese, and rhenium compounds dispersed in a low-melting (mp <150 °C) quaternary phosphonium salt, such as Bu_4PBr, have been found effective for the selective synthesis of (a) methanol, (b) ethanol, and (c) their acetate esters, directly from CO/H_2. For the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr catalyst precursor, interrelationships have been developed linking the alcohol–acetate ester product composition with the competing steps of CO hydrogenation to C_1 products (methanol), homologation (to ethanol and propanol) and carbonylation reactions (generating acetic acid). The ruthenium and cobalt carbonyl species present during these particular syntheses include $[HRu_3(CO)_{11}]^-$, $[Ru(CO)_3Br_3]^-$, and $[Co(CO)_4]^-$. Spectroscopic, kinetic and ^{13}C-labeling studies have been used to gain a better understanding of the mechanisms of the competing steps. Conditions have also been established where acetic acid is prepared directly from CO/H_2 as the predominant oxygenate product in 68 wt % selectivity.

Introduction

The inherent advantages of applying homogeneous metal catalysis techniques to organic synthesis lie primarily in the ability of this class of catalyst to achieve a high degree of selectivity and good reproducibility and to provide pure products in high yields.[1] Without sacrificing these attractive features, the scope of homogeneous catalysis has in recent years been extended by the design of techniques that also facilitate efficient product–catalyst separation without inducing catalyst decomposition. These alternative approaches have included: (a) the use of immobilized transition-metal catalysis where the active metals are bonded to functionalized organic polymers or inorganic supports;[2–6] (b) organometallic phase-transfer catalysis where catalyst and product ultimately reside in different phases;[7–10] and(c) restraint of the catalysts by semipermeable membranes.[11,12]

An alternative approach that appears to have received less attention is the use of molten salts as the reaction media. Molten salts display excellent heat transfer characteristics, and through their ability to dissolve a broad range of metals, oxides, salts, etc., high reaction rates are possible in the homogeneous phase.[13] Where reaction occurs at the melt interface, the ability to present a renewable surface may allow one to avoid many of the problems of conventional heterogeneous catalysis. Molten salts have been used in oxidation,[14] transalkylation,[15] and Fischer–Tropsch syntheses.[16] Industrial applications include coal beneficiation, glass manufacture, and heat treatment of metals, as well as SO_2 oxidation[13] and the chlorination of hydrocarbons.[17]

In the field of catalysis, most notable is the work of Parshall, who used low-melting, tetraalkylammonium salts of $SnCl_3^-$ and $GeCl_3^-$ anions as solvents for the platinum-catalyzed hydrogenation and hydroformylation of olefins, as well as for the selective hydrogenation of dienes and trienes.[18] Subsequently, we have employed ligand-stabilized palladium(II) chlorides dispersed in quaternary group 5B salts of trichlorostannate (II) as catalysts for the regioselective carbonylation of α-olefins to linear fatty acid derivatives.[19]

As part of our present research program into the selective production of aliphatic oxygenates from synthesis gas using molten salts as reaction media,[20–22] we describe here the synthesis of C_1–C_3 alcohols and their acetate esters (eq 1) directly from CO/H_2 using a series of ruthenium-containing bimetallic "melt" catalysts.

$$CO + H_2 \rightarrow C_nH_{2n+1}OH + C_nH_{2n+1}OAc \tag{1}$$

By judicious choice of catalyst components this class of melt catalyst may be used to selectively prepare as the predominant product: (a) methanol, (b) ethanol, and (c) their acetate esters, as well as mixtures thereof. For the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr catalyst precursor, interrelationships have been developed linking alcohol–ester product composition, first, with the competing reactions of CO hydrogenation to C_1-oxygenate, homologation and carbonylation, and, secondly, with the ruthenium and cobalt carbonyl species responsible for these differing reaction steps.

Results

General Synthesis. A variety of C_1–C_3 alcohol and acetate ester combinations may be generated by the applications of ruthenium bimetallic "melt" catalysis. Table I, experiments 1–10, illustrates the general scope of these

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syntheses. The catalyst precursor may comprise three components: (a) a ruthenium source, typically ruthenium(IV) oxide hydrate, ruthenium(III) acetylacetonate, and triruthenium dodecacarbonyl; (b) a second metal selected from the group including halogen-free titanium, zirconium,[23] cobalt,[24] manganese, and rhenium[25] compounds; (c) a low-melting (mp <150 °C) quaternary phosphonium salt such as tetrabutylphosphonium bromide and heptyltriphenylphosphonium bromide. Catalyst combinations are generally heated under synthesis gas to at least 150 °C and 35 bar[26] in order to achieve the desired CO hydrogenation. The following may be seen from an inspection of Table I:

(1) Ethanol may constitute up to 61 mol % of the alkanol product with ruthenium–titanium alkoxide catalyst combinations (experiment 1);[23] the C_1–C_3 alkanols may comprise up to 65 wt % of the total product and liquid yield increases exceed 200% (experiment 2).

(2) A balanced mix of C_1–C_3 alcohols and their acetate esters may be prepared in high yields and up to 91 wt % selectivity using various ruthenium–cobalt catalysts—illustrated here by experiments 5–7.[24]

(3) Methanol will be the predominant product fraction when the catalyst is composed of ruthenium plus a halogen-free rhenium or manganese compound.[25] Starting from RuO_2–$Re_2(CO)_{10}$/Bu_4PBr (experiment 8), methanol selectivity in the liquid product is 85 wt % and the turnover frequency is 24 mol of MeOH/g-atom Ru/h.

(4) The addition of certain solvents may lead to further changes in product composition.[27] Ethyl acetate, for example, is the predominant fraction when *p*-dioxane is the added solvent (experiment 10). Alkyl acetates make up to 67% of the organic liquid product.

Ruthenium–Cobalt Catalysis. A more detailed study into the mechanism of ruthenium bimetallic "melt" catalysis has been undertaken for the ruthenium–cobalt combination. Specifically, for the triruthenium dodecacarbonyl–dicobalt octacarbonyl couple, dispersed in tetrabutylphosphonium bromide, we have defined the experimental limits of this catalysis, demonstrated multiple catalyst recycle,[24] and most importantly, identified some of the relationships linking catalyst productivity, alcohol–ester carbon distributions, and certain key operating parameters with the catalytically active metal carbonyl species present in these reaction media.

Even a cursory examination of the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr catalyst performance (Table I) suggests that there are a number of competing reactions taking place during CO hydrogenation, including CO hydrogenation to methanol, alcohol homologation, carbonylation, acid esterification, and water gas shift. These reactions are illustrated by, but not limited to eq 2–6.

$$CO + 2H_2 \rightarrow CH_3OH \quad (2)$$

$$CO + 2H_2 + CH_3OH \rightarrow C_2H_5OH + H_2O \quad (3)$$

$$CO + CH_3OH \rightarrow CH_3COOH \quad (4)$$

$$CH_3COOH + ROH \rightarrow CH_3COOR + H_2O \quad (5)$$

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (6)$$

A typical reaction profile for the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr catalyst precursor is illustrated in Figure

Table I. Alkanols Plus Acetate Esters from Synthesis Gas[a]

expt	cat. precursor	quaternary salt	mp, °C	product yield,[b] mmol						total liquid yield,[d] wt %
				MeOH	EtOH	PrOH	MeOAc	EtOAc[c]	PrOAc[c]	
1	RuO_2–$Ti(acac)_2(OBu)_2$	Bu_4PBr	100	110	193	16	10	20	9	169
2	RuO_2–$Ti(OMe)_4$	Bu_4PBr	100	179	231	24	13	19	8	239
3	RuO_2–$Ti(acac)_2(OBu)_2$	Bu_4PI	96	21	31	3	1	2	1	33
4	RuO_2–$H_2ZrO_2(OAc)_2$[e]	Bu_4PBr	100	208	146	12	7	3	6	230
5	$Ru(acac)_3$–$Co(acac)_3$[e]	Bu_4PBr	100	93	81	25	29	28	12	128
6	RuO_2–$Co(acac)_3$[e]	Bu_4PBr	100	84	161	60	21	59	24	215
7	$Ru_3(CO)_{12}$–$Co_2(CO)_8$	Bu_4PBr	100	77	168	56	25	63	31	230
8	RuO_2–$2Re_2(CO)_{10}$	Bu_4PBr	100	291	22		1	1		85
9	RuO_2–$8MnCO_3$	Bu_4PBr	100	280	5		2	1		85
10	RuO_2–$^1/_4Co_2(CO)_8$[f]	$C_7H_{15}Ph_3PBr$	179		7		8	49	5	*g*

[a] Typical operating conditions: 220 °C, 435 bar constant pressure, CO/H_2 (1/1). Catalyst charge: Ru, 2–4 mmol; quaternary salt, 10.0 g. [b] Liquid product analysis by GLC, also detected: water, alkyl formates, butanols, acetaldehyde, 2-methyl-1,3-dioxolane, dialkyl ethers, glycol monoalkyl ethers and ethylene glycol; CO_2 and CH_4 present in the product gas samples, along with larger quantities of unreacted CO/H_2. [c] Small quantities of methyl propionate and ethyl propionate present in these fractions. [d] Liquid yield (wt %) calculated basis total catalyst charge. [e] Operating pressure, 276 bar. [f] Run in *p*-dioxane solvent, operating pressure, 551 bar. [g] Product also contains substantial quantity of acetic acid, 27 mmol; *p*-dioxane solvent recovered quantitatively unchanged.

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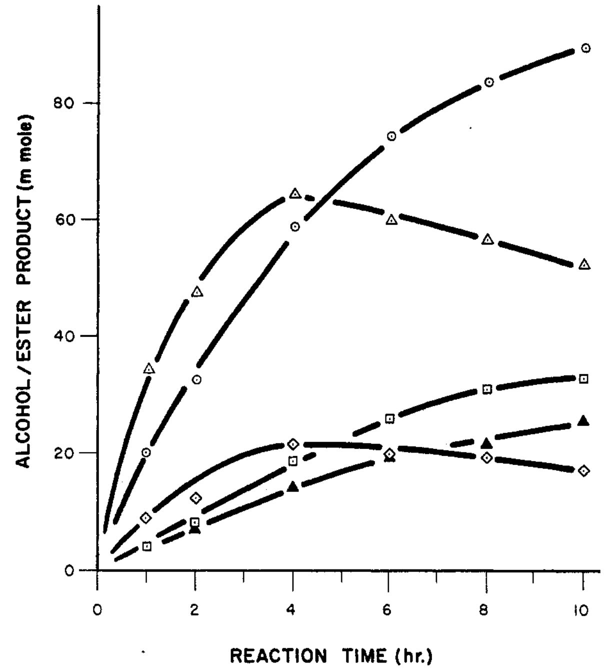

Figure 1. Alcohols and esters from synthesis gas—typical reaction profile. Catalyst charge: Ru, 4.0 mmol; Co, 4.0 mmol, Bu_4PBr, 10.0 g. Reaction conditions: 220 °C; 276 bar; H_2/CO, 1/1. Product profile: methanol, △; ethanol, ○; propanol, ▲; methyl acetate, ◇; ethyl acetate, □. Data point sets for each reaction time (1→10 h) illustrated here were determined in separate experiments by analysis of the total liquid + gas products. Reproducibility was checked in duplicate runs.

1. The important features of these data are as follows:

(a) The predominant initial reaction is methanol formation.

(b) Homologation to C_2–C_3 alcohol becomes an increasingly important competing reaction so that ethanol eventually becomes the predominant fraction in the latter stages, while total methanol content actually declines.

(c) Acetate ester formation is notably slower than alcohol formation, but again the methyl ester is the initial predominant ester fraction while later it is ethyl acetate.

(d) Acetic acid is present in only trace quantities under these particular operating conditions.

Replotting the same data in terms of total methanol formation (including formation of all MeOH derivatives) and total carbonylation productivity leading to acetic acid and its acetate esters, as well as total homologation to higher alcohols, we find (see Figure 2) that the ratio of total methanol formations, vs. carbonylation productivity remains constant, within experimental error, throughout this experimental sequence (1:0.24 → 1:0.22, respectively). On the other hand, there is a substantial decrease in the ratio of total methanol to total homologation productivity (from 1:0.34 → 1:0.64, respectively, in Figure 2) as a function of time. Furthermore, in related experimental series, these changes in the ratio of methanol formation to homologation activity are themselves found to be sensitive to the choice of operating parameters—particularly temperature and syngas composition, as well as initial Ru and Co concentrations. A plausible explanation for these observations is that the ethanol fractions are being generated via two reaction paths—namely, methanol homologation (eq 3) and direct synthesis from CO/H_2 (vide infra). Alternative explanations for these data include (a) differing rates of catalyst deactivation (Ru vs. Co) and (b) changes in reaction parameters (solvent media etc) during the course of these synthesis which affect each catalyst moiety differently. However, both batch[24] and continuous[22] Ru–Co recycle studies exhibit no significant problems with catalyst deactivation (MeOH productivity ±5% upon recycle). Furthermore, the addition of even 60 mmol of methanol at the start of experimental series, such as that depicted in Figure 1, leads to suppression of MeOH productivity only by a factor of ca. 40%.

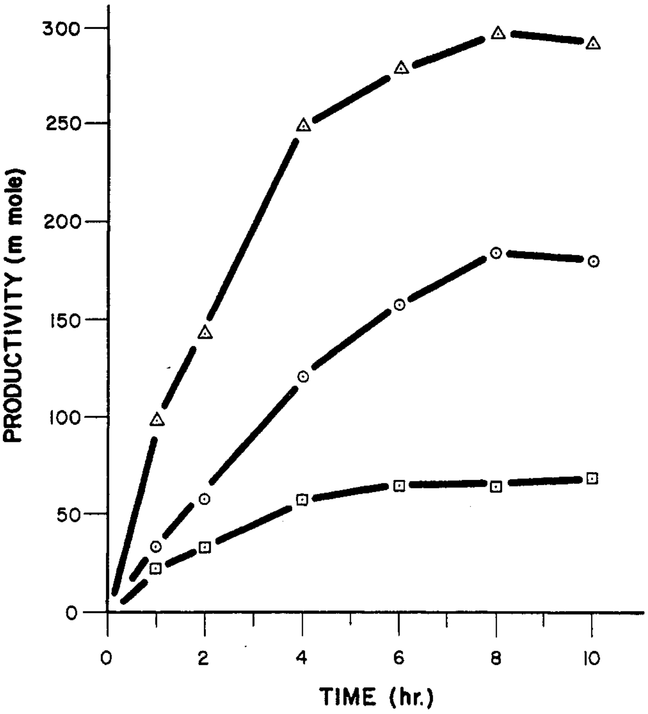

Figure 2. Alcohols and esters from synthesis gas: total methanol formation, △; homologation productivity (including EtOH, PrOH, EtOAc, and PrOAc formation), ○; carbonylation productivity (including HOAc and ROAc formation), □.

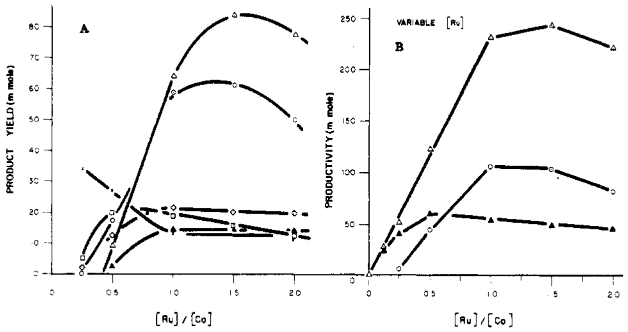

Figure 3. Alcohols and esters from synthesis gas—effect of [Ru]. (A) Catalyst charge: Co, 4.0 mmol; Ru, 0 → 8.0 mmol; Bu_4PBr, 10.0 g (reaction conditions as per Figure 1). Product profile: methanol, △; ethanol, ○; propanol, ▲; methyl acetate, ◇; ethyl acetate, □; acetic acid, ×. (B) Total methanol formation, △; homologation productivity, ○; carbonylation productivity, ▲; as defined in Figure 2.

In order to determine which catalytically active species is responsible for each of these oxygenated products (Figure 1), we have also examined product compositions as a function of the individual ruthenium–cobalt carbonyl derivatives present during each CO hydrogenation sequence.

Catalyst Composition Studies. The importance of $Ru_3(CO)_{12}$–$Co_2(CO)_8/Bu_4PBr$ catalyst composition has been examined first as a function of varying ruthenium concentrations. Figure 3 illustrates the effect of variations in [Ru] upon C_1–C_3 alcohol productivity and the generation of C_1–C_3 alkyl acetates. All other reaction parameters, including [Co], remained constant. The important con-

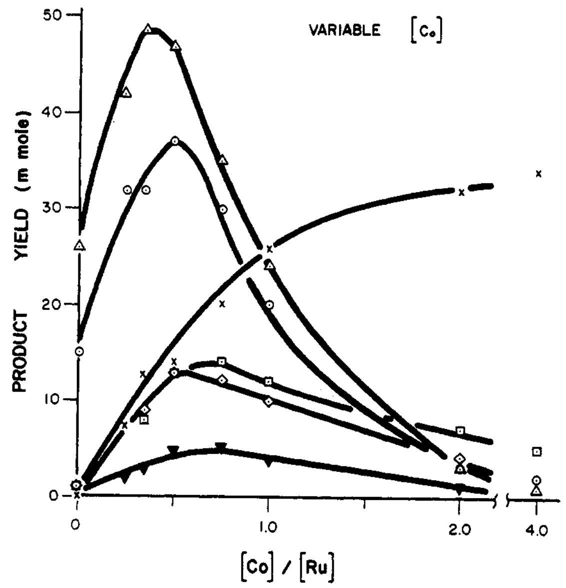

Figure 4. Alcohols and esters from synthesis gas—effect of [Co]. Catalyst charge: Ru, 1.0 mmol; Co, 0 → 4.0 mmol; Bu_4PBr, 10.0 g (reaction conditions as per Figure 1; designations as per Figure 3A).

clusions drawn from an inspection of Figure 3A are as follows:

(a) No aliphatic oxygenates (including methanol) are formed in the absence of the ruthenium carbonyl component.

(b) Acetic acid is the predominant product when the initial Ru/Co molar ratios are <0.5. Selectivity to this acid may reach 68 wt % of the liquid product under these standard operating conditions; the product solutions show strong carbonyl spectra characteristic of $[Co(CO)_4]^-$ (vide infra).

(c) Raising the Ru/Co molar ratio increases C_1–C_3 alcohol activity.

Maximum methanol formation is achieved with a [Ru]/[Co] ratio of ca. 1.5. Although ruthenium "melt" catalysts alone are known[20] to generate ethanol, maximum yields of ethanol are seen here at Ru/Co ratios of 1 → 2. Similar preferred ratios have recently been reported by Doyle,[28] during methanol homologation studies catalyzed by mixed Ru–Co clusters.

Replotting the same data in terms of total methanol, homologation, and carbonylation productivity (see Figure 3B) we find that while homologation activity peaks at Ru/Co molar ratios of close to unity and methanol formation is initially first order in [Ru], the carbonylation activity leading to acetic acid and its esters changes substantially less with increased ruthenium content (this is particularly true over the Ru/Co range 0.5–2.0). We conclude then that acetic acid/ester generation is relatively insensitive to ruthenium catalyst concentration so long as the rate of methanol formation is significantly faster than carbonylation activity. Increasing cobalt concentrations, on the other hand, do lead to substantial improvements in carbonylation productivity (see Figure 4). Acetic acid is again the major product fraction at Co/Ru ratios ≥1, and although C_1–C_3 alcohols are generated in the absence of cobalt,[20] ethanol formation is again maximized at Co/Ru ratios of less than unity.

There are a number of other interconnecting factors that influence the performance of the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr—as in related ruthenium "melt" catalysts.[22]

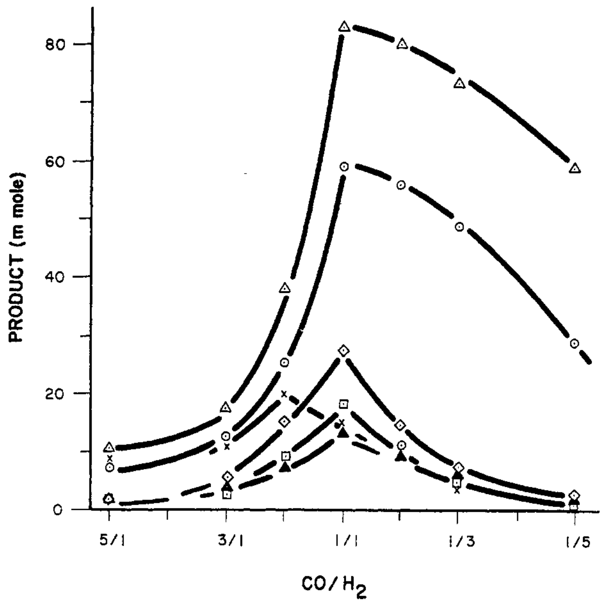

Figure 5. Alcohols and esters from synthesis gas—effect of syngas composition. Catalyst charge: Ru, 4.0 mmol; Co, 4.0 mmol, Bu_4PBr, 10.0 g (reaction conditions as per Figure 1; (designations as per Figure 3A).

Figure 5 shows how the synthesis gas composition can change the total alcohol–ester productivity and composition. We find the following:

(a) Carbonylation reactions—such as the formation of HOAc—are favored by a CO-rich environment (e.g., where the CO/H_2 ratio is 2/1) even while the total liquid productivity drops off precipitously in a CO-rich environment.

(b) Ester formation—particularly MeOAc formation—is maximized with a CO/H_2 ratio of close to unity. This is an approximate accord with the overall stoichiometry of this synthesis (eq 7).

$$3CO + 4H_2 \rightarrow CH_3COOCH_3 + H_2O \qquad (7)$$

(c) Hydrogen-rich gas by contrast tends to lower the ruthenium catalyst thermal stability (particularly above 240 °C[22]) and to favor hydrogenation over carbonylation activity. The product liquids thereby become richer in methanol and the ethanol/methanol mole ratio drops sharply (from 0.72 to 0.49 in Figure 5) as the H_2/CO ratio is raised from 1/1 to 5/1.

Solution Spectra. The typical crude product solutions from these triruthenium dodecacarbonyl–dicobalt octacarbonyl/tetrabutylphosphonium bromide catalyzed CO hydrogenations to C_1–C_3 alcohols and their acetate esters display three band sets in the metal carbonyl spectral region (see Figure 6). The strong band at ca. 1888 cm^{-1} is characteristic[29] of $[Co(CO)_4]^-$. The group of bands at 1955, 1990, and 2017 cm^{-1} is characteristic[30] of the hydridoruthenium carbonyl anion, $[HRu_3(CO)_{11}]^-$. The third set is a pair of bands at 2040 and 2115 cm^{-1} that is consistent[31] with the presence of $[(Ru(CO)_3Br_3]^-$.

Changes in these spectra do occur with changes in the ruthenium—cobalt catalyst composition. In particular, where catalyst solutions contain ruthenium and cobalt in molar ratios that equal or exceed unity, all three band sets are generally observed, characteristic of $[Co(CO)_4]^-$, $[HRu_3(CO)_{11}]^-$, and $[Ru(CO)_3Br_3]^-$.

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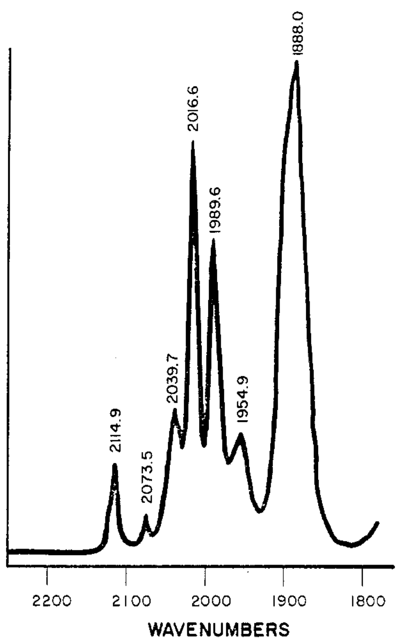

Figure 6. Alcohols and esters from synthesis gas—Spectrum of typical product solution. (catalyst, $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr; catalyst charge and reaction conditions as per Figure 1).

Where the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr combination is such that the Ru/Co molar ratio is less than unity, only $[Co(CO)_4]^-$ and $[Ru(CO)_3Br_3]^-$ are normally seen. Comparing the absorbances of these spectra with standard solutions of $[Co(CO)_4]^-$, $[Ru(CO)_3Br]^-$, and $[HRu_3(CO)_{11}]^-$, it is evident that most of the available cobalt and ruthenium can be accounted for on the basis of these three species. ^1H NMR spectra of the same product solutions exhibit hydride resonances at −12.6 ppm—consistent[30] with $[HRu_3(CO)_{11}]^-$—plus a second, weaker band at −11.3 ppm ascribed[32] to $HCo(CO)_4$. This cobalt hydride is expected to be extensively ionized[33] in the polar tetrabutylphosphonium bromide salt. ^{31}P spectroscopy shows the continued presence of Bu_4P^+, but no Bu_3P, phosphine oxide, or phosphine-containing cobalt or ruthenium species. Chromatographic separation of the crude product solution leads to the isolation of small quantities of $Ru_3(CO)_{12}$ plus impure $[Ru(CO)_3Br_2]$.

We conclude that most of the ruthenium and cobalt present in this bimetallic "melt" catalyst system exists as separate and identifiable metal carbonyl anionic entities. Mixed-metal carbonyl clusters, if present, do not appear in high concentrations.

Examining also the C_1–C_3 alcohol and acetate ester productivity of the $Ru_3(CO)_{12}$–$Co_2(CO)_8$/Bu_4PBr catalyst as a function of the concentrations of the three metal carbonyls $[Co(CO)_4]^-$, $[HRu_3(CO)_{11}]^-$, and $[Ru(CO)_3Br_3]^-$, we find the following in the case of varying [Ru] (Figure 7):

(a) A rapid increase in methanol productivity with increase in $[Ru(CO)_3Br_3]^-$ concentration as measured by its characteristic band at 2115 cm^{-1}.

(b) No significant increase in productivity with increase in $[HRu_3(CO)_{11}]^-$ concentrations.

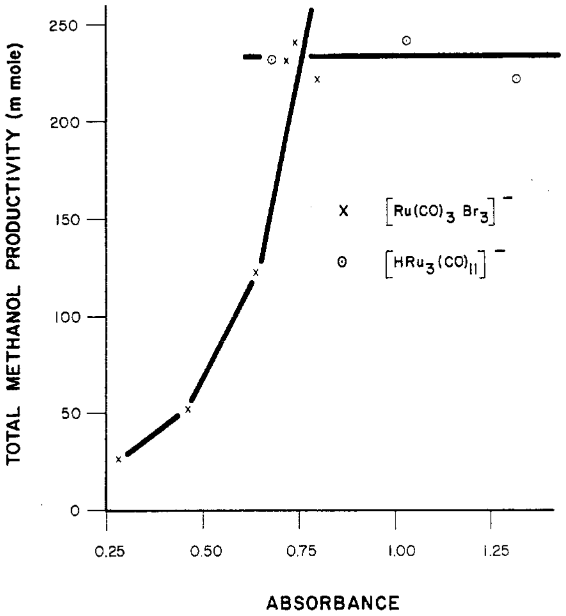

Figure 7. Alcohols and esters from synthesis gas—methanol productivity vs. $[Ru(CO)_3Br_3]^-$ andd $[HRu_3(CO)_{11}]^-$ concentration (catalyst charge and reaction conditions as per Figure 3; Ru, 0 → 8.0 mmol).

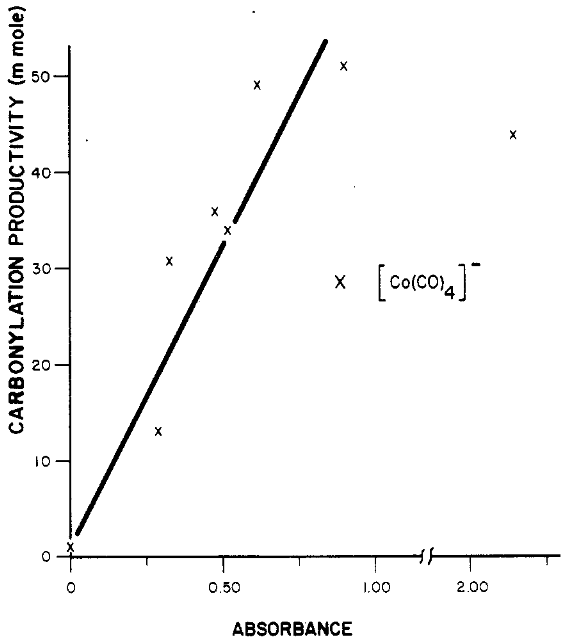

Figure 8. Acetic acid + acetate esters from synthesis gas—carbonylation productivity vs. $[Co(CO)_4]^-$ concentration (conditions as per Figure 4).

Again higher ruthenium concentrations do favor the presence of $[HRu_3(CO)_{11}]^-$, but this does not lead to an accompanying increase in alcohol–ester productivity. As noted above, total $[HRu_3(CO)_{11}]^-$ plus $[Ru(CO)_3Br_3]^-$ content can account for nearly all the ruthenium charged. Although the interrelationships linking these ruthenium carbonyls are now well recognized (e.g., eq 8), there are alternative routes[34] to the generation of $[HRu_3(CO)_{11}]^-$.

$$Ru_3(CO)_{12} + H_2 + Br^- \rightarrow [HRu_3(CO)_{11}]^- + [Ru(CO)_3Br_3]^- \quad (8)$$

In a related series of experiments where conditions favor the formation of acetic acid and its acetate esters (see Figure 4), varying the cobalt concentration at fixed [Ru] results both in an increase in cobalt tetracarbonyl anion concentration in the crude product and in an increase in carbonylation activity as determined by total HOAc +

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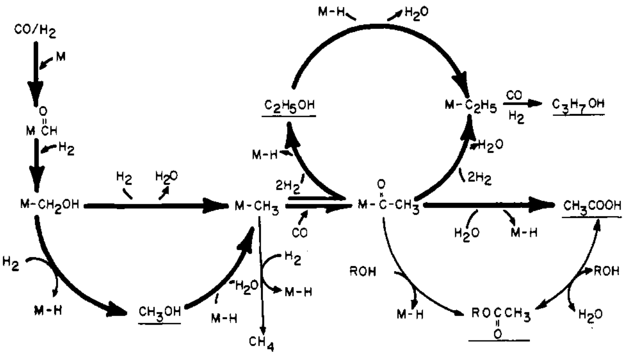
Scheme I. Formation of Methanol, Ethanol, Propanol, Acetic Acid, and Its Acetate Esters from Synthesis Gas



ROAc product. The approximately linear correlation between $[Co(CO)_4]^-$ concentration, as measured by its characteristic absorption at 1888 cm^{-1}, and total carbonylation productivity is illustrated in Figure 8. This relationship holds true only, however, for operating conditions where methanol production clearly exceeds total carbonylation, in particular, where the crude product liquid contains excess methanol (Figure 4). For a series of different initial ruthenium concentrations, these conditions are generally satisfied only when [Ru]/[Co] ratios exceed unity.

Discussion

CO hydrogenation catalyzed by Ru–Co bimetallic "melt" catalysts may lead to the formation of four classes of product: (a) alcohols, including methanol, ethanol, and propanol; (b) esters, mainly methyl acetate and ethyl acetate; (c) acids, acetic acid plus smaller quantities of propionic acid; (d) hydrocarbons, methane (see Experimental Section).

Our spectral results indicate that the soluble metal carbonyl species associated with the formation of the major oxygenated product fractions are likely to be: methanol formation, related to the presence of $[Ru(CO)_3Br_3]^-$, see Figure 7; acetic acid, $[Co(CO)_4]^-$, see Figure 8; ethanol, a combination of two or more monometallic ruthenium and cobalt species. Formation of each of these classes of oxygenated products may be best understood within the context of an overall reaction schematic.

Methanol. In the case of methanol formation (eq 2), while this alcohol is observed early in all catalytic cycles with the $Ru_3(CO)_{12}$–$Co_2(CO)_8/Bu_4PBr$, the decrease in methanol content later in the synthesis (Figure 1) suggests reentry of the methanol into the catalytic cycle. This general observation (for a series of different initial cobalt and ruthenium concentrations), together with the demonstrated chemical phenomena of Figures 1 → 8, may be accommodated within the framework of the proposed reaction pathways of Scheme I. Formation of methanol is initially first-order dependent upon [Ru] (see Figure 3B) but less than first order in total [Ru + Co] concentration under these same operating conditions. Coupled with the approximate linear sensitivity to partial pressure of carbon monoxide (Figure 9), these data are in accord with a ruthenium-catalyzed CO insertion mechanism for methanol formation—possibly involving the formation of formyl-[35,36] and (hydroxymethyl)ruthenium (as well as CH_3ORu) intermediates as depicted in Scheme I (both methyl formate and ethylene glycol are present as minor products, Table I, in accord with a mechanism of CO hydrogenation involving both (hydroxymethyl)- and methoxyruthenium intermediates). Figure 7 illustrates the qualitative link between total MeOH productivity and the presence of $[Ru(CO)_3Br_3]^-$. There remains, however, unanswered questions regarding whether $[Ru(CO)_3Br_3]^-$ is the *only* metal carbonyl precursor associated with the formation of methanol. Methanol is readily generated by ruthenium "melt" catalysis in the absence of cobalt at somewhat similar rates (5×10^{-3} s^{-1} at 220 °C[20]) to those reported here (e.g., 6.2×10^{-3} s^{-1}, Figure 1[37]). Figure 4, nevertheless, clearly shows an initial improvement in MeOH yield upon the addition of dicobalt octacarbonyl. We conclude, then, there may be other catalytically active, but spectroscopically undetectable, ruthenium or Ru–Co species in these solutions.

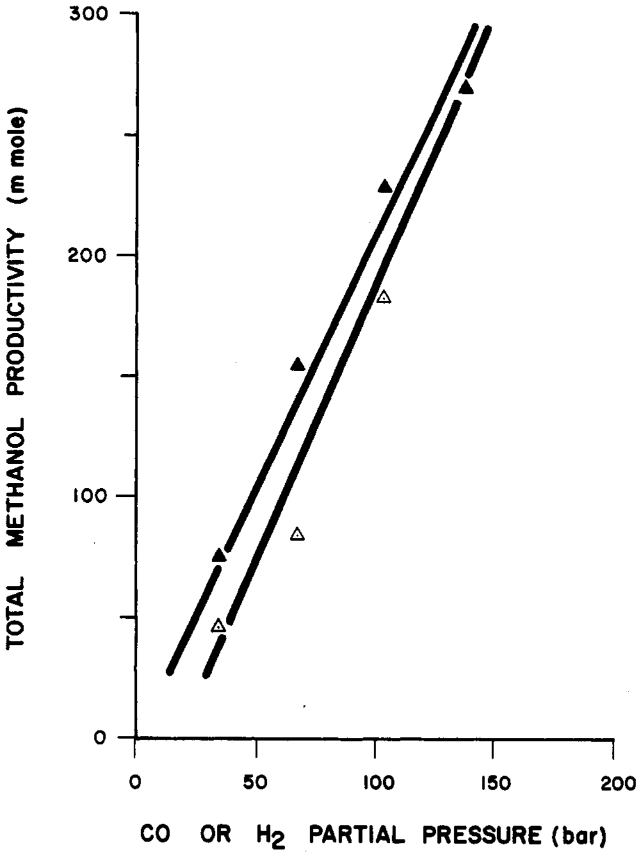


Figure 9. Methanol from synthesis gas—effect of CO and H_2 partial pressures. (catalyst charge as per Figure 1); CO partial pressure 138 bar, variable H_2 partial pressure, △; H_2, partial pressure 138 bar, variable CO partial pressure, ▲.

Ethanol. A number of researchers have examined ruthenium–cobalt catalyzed methanol homologation to ethanol.[28,38–40] Doyle concludes[28] that the ruthenium and cobalt moieties act independently, with cobalt species responsible for the formation of C_2-oxygenates like acetaldehyde and ruthenium reducing the aldehyde intermediate to ethanol. In previous papers in this series we reported[20] that ruthenium alone (in the absence of cobalt, i.e., using $Ru_3(CO)_{12}/Bu_4PBr$) will catalyze ethanol formation. However, the rate of ethanol formation is sig-

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Table II. Alkanols and Acetate Esters from Synthesis Gas Plus Added $^{13}CH_3OH$[a]

	product yield, mmol	^{13}C enrichment	
		position	factor[b]
CH_3OH	41	*C—O	
CH_3CH_2-OH	34	*C—C—O	6:0
CH_3CO-OCH_3	14	*C—C(=O)—O—C*	10:0:3
CH_3CO-OCH_2CH_3	8	*C—C(=O)—O—C—C*	10:0:0:7

[a] Reaction conditions: 220 °C, 276 bar constant pressure, CO/H_2 (1/1), 2 h. Catalyst charge: Ru, 4.0 mmol; Co, 4.0 mmol; Bu_4PBr, 10.0 g; 90% ^{13}C-labeled CH_3OH, 0.5 g, added before run. [b] Enrichment factor basis ^{13}C natural abundance.

nificantly faster in the presence of cobalt (turnver frequency 1.6×10^{-3} s^{-1} for Ru alone[20] vs. 4.6×10^{-3} s^{-1} in Figure 4), and only with the Ru–Co combination does ethanol become the major product fraction (see Figure 1). Even so, under our CO hydrogenation conditions— with CO-rich syngas (Figure 5)—acetaldehyde is never more than a trace product. Mixed ruthenium–cobalt carbonyls are now well documented,[28,40,41] but in this work most of the ruthenium and cobalt can be accounted for on the basis of the species $[Co(CO)_4]^-$, $[HRu(CO)_{11}]^-$, and $[Ru(CO)_3Br_3]^-$. There is at this stage no direct spectroscopic evidence for the formation of mixed-metal carbonyls.

The results of ^{13}C-labeling studies, using small quantities of 90% ^{13}C-enriched MeOH at the start of the run, are illustrated in Table II. The ethanol enrichment is only at the terminal methyl, consistent with a substantial portion of this product coming from methanol homologation[38] (eq 3). Decreases in the ratio of methanol to homologation productivity as a function of time (Figure 2) may, however, at least in part be indicative of ethanol generation both by homologation and direct synthesis—as outlined in Scheme I. Alkylmetal species[34,38,42] are the proposed common intermediates. Typical distributions of C_1–C_3 alcohol products (Figures 1 and 2) do not follow the Schultz–Flory relationship,[43] but this is not surprising in view of our kinetic and spectroscopic evidence suggesting that the C_1–C_2 alcohol fractions are coming from different catalytically active intermediates.

Acetic Acid. Acetic acid is preferentially generated with the $Ru_3(CO)_{12}$–$Co_2(CO)_8/Bu_4PBr$ catalyst at high cobalt/ruthenium and high CO/H_2 ratios (see Figures 3, 4, and 5, respectively). Under these preferred conditions, carbonylation is apparently rapid relative to hydrogenation activity and much of the methanol primary product is converted to HOAc, as outlined in Scheme I. The $[Co(CO)_4]^-$ anion is, under these HOAc preferred conditions, present in significant concentrations together with smaller quantities of $HCo(CO)_4$. Most of the cobalt charged at the beginning of these experiments can be accounted for on the basis of these cobalt carbonyls, and the correlation of Figure 8 suggests it is these carbonyls or the derivatives thereof that are responsible for the carbonylation step leading to acetic acid formation (see Scheme I).

^{13}C data for the enriched acetate ester byproducts (Table II) are also in accord with Scheme I. The enrichment pattern for ethyl acetate is (a) in the case of the ethyl group similar to that found for the coproduct ethanol and (b) for the acetate fraction consistent with acetic acid generation via the carbonylation of intermediate (enriched) methanol. Likewise, the enrichment pattern for coproduct methyl acetate (Table II) is in accord with HOAc formation via enriched methanol carbonylation.

Acetic acid has previously been prepared directly from synthesis gas over a variety of heterogeneous, transition-metal, catalysts[44-46] and by acid-induced reductive coupling of carbon monoxide.[47] The data of Figures 3 and 4 illustrate how acetic acid may also be generated (in >60% selectivity in the liquid product) directly from CO/H_2 by the application of ruthenium "melt" catalysis.[48] Work on new potential applications of this chemistry is continuing.

Experimental Section

Triruthenium dodecacarbonyl, dicobalt octacarbonyl and related metal oxides, salts, and complexes were purchased from outside suppliers. Tetrabutylphosphonium bromide was purchased from Aldrich Chemical Co. and used as received. Synthesis gas was supplied by Big Three Industries in various proportions of carbon monoxide and hydrogen. All high-pressure experiments were conducted in 450- and 845-mL capacity Aminco pressure reactors constructed of 316 stainless steel, fitted with heating and agitation means, and hooked to large, high-pressure, synthesis gas reservoirs. Each reactor was fitted with interchangeable Pyrex glass liners.

The extent of reaction and distribution of products were determined by gas–liquid chromatography using a 6 ft × $^1/_8$ in. column of porous polymer programmed from 140 to 260 °C (20 cm^2/min He). C_1–C_3 alcohols and their acetate ester products were isolated by fractional distillation in vacuo or by GLC trapping and identified by one of the following techniques: GLC, FTIR, NMR, and elemental analyses.

C_1–C_3 Alcohol–Acetate Ester Synthesis. A mixture of triruthenium dodecacarbonyl (0.852 g, 4.0 mmol of Ru) and dicobalt octacarbonyl (0.684 g, 4.0 mmol of Co) dispersed in tetrabutylphosphonium bromide (10.0 g) is transferred in a glass liner under N_2 purge to a 450-mL capacity precursor reactor equipped with heating and means of agitation. The reactor is sealed, flushed with a mixture of carbon monoxide and hydrogen (1/1 molar), and pressured to 69 bar with the same carbon monoxide–hydrogen. The reactor is heated to 220 °C, with rocking, the pressure raised to 276 bar by addition of the same (1/1) carbon monoxide/hydrogen mixture from a large surge tank, and the reactor held at temperature for 6 h. Pressure is maintained at ca. 276 bar by incremental additions of carbon monoxide/hydrogen from the surge tank.

On cooling, a typical gas sample is taken and the excess gas is removed. The reddish brown liquid product (24.5 g) is analyzed by GLC and Karl–Fischer titration and the following results were obtained:[49] 26.7 wt % ethanol; 14.8 wt % methanol; 9.1 wt % *n*-propanol; 1.3 wt % water; 11.2 wt % methyl acetate; 17.4 wt % ethyl acetate; 7.0 wt % propyl acetate; 6.0 wt % acetic acid. The liquid yield increase is $(24.5 - 11.5)/11.5 \times 100 = 113\%$.

The alkanol and acetate ester product fractions are recovered from the crude liquid product by fractional distillation in vacuo. The dark red liquid residue resolidifies upon cooling. Analyses of typical gas samples show the presence of[49] 39% hydrogen, 35% carbon monoxide, 19% carbon dioxide, and 6% methane.

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Gonzales, R. D. Czimskey, R. white, and D. W. White for experimental assistance and J. M. Schuster and C. L. LeBas for FTIR and NMR data.

Registry No. RuO_2, 12036-10-1; $Ru(acac)_3$, 14284-93-6; $Ru_3(CO)_{12}$, 15243-33-1; $Ti(acac)_2(OBu)_2$, 16902-59-3; $Ti(OMe)_4$, 992-92-7; $H_2ZrO_2(OAc)_2$, 14311-93-4; $Co(acac)_3$, 21679-46-9; CO, 630-08-0; $Co_2(CO)_8$, 10210-68-1; $Re_2(CO)_{10}$, 14285-68-8; $MnCO_3$, 598-62-9; Bu_4PI, 3115-66-0; $C_7H_{15}Ph_3PBr$, 13423-48-8; PrOH, 71-23-8; MeOAc, 79-20-9; EtOAc, 141-78-6; PrOAc, 109-60-4; MeOH, 67-56-1; Bu_4PBr, 3115-68-2; AcOH, 64-19-7; EtOH, 64-17-5.

Organometallic Compounds of the Lanthanides. 17.[1] Tris[(tetramethylethylenediamine)lithium] Hexamethyl Derivatives of the Rare Earths

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The trichlorides of yttrium, lanthanum, and the lanthanides react with methyllithium in diethyl ether in the presence of tetramethylethylenediamine (tmed) to give the complexes $[Li(tmed)]_3[Ln(CH_3)_6]$ with Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. From the reaction of lutetium tri-*tert*-butoxide, tmed, and *tert*-butyllithium in pentane, $[Li(tmed)_2][Lu(t\text{-}C_4H_9)_4]$ has been obtained. The new compounds have been characterized by elemental analyses and IR and NMR spectra. The structure of $[Li(tmed)]_3[Ho(CH_3)_6]$ has been elucidated through complete X-ray analysis. The crystals are rhombohedral with $a = 1280.7$ (20) pm, $\alpha = 79.84$ (13)°, space group $R\bar{3}c$, $Z = 2$, D(calcd) = 0.96 g cm^{-3}, $R = 0.050$, and 1535 observed reflections. The potential of methylating α,β-unsaturated aldehydes and ketones has been explored for $[Li(tmed)]_3[Pr(CH_3)_6]$ and $[Li(tmed)]_3[Sm(CH_3)_6]$, and it was found that 1,2 methylation is favored over 1,4 addition.

Introduction

The first description of an organometallic compound of a rare-earth element, the synthesis of $Sc(C_2H_5)_3$ and $Y(C_2H_5)_3$ in 1938, was an error,[2] and the first attempts to prepare phenyl derivatives of lanthanum and some lanthanides by Gilman and co-workers failed. Biphenyl was the only reaction product isolated from the reactions of $LaCl_3$ with LiC_6H_5 in ether or from La with diphenylmercury at elevated temperatures in a sealed tube.[3] Wilkinson and Birmingham prepared the first organometallic compounds of the rare earths, the tricyclopentadienyl complexes of Sc, Y, La, Ce, Pr, Nd, Sm, and Gd.[4] Fourteen more years were required to demonstrate the synthesis of $Sc(C_6H_5)_3$, the first "homoleptic" η^1-bonded organometallic compound of a rare-earth element.[5] The reaction of phenyllithium with $LaCl_3$ or the trichlorides of some lanthanides did not give analogous derivatives. In the cases of $LaCl_3$ and $PrCl_3$, compounds of the type $Li[Ln(C_6H_5)_4]$ were formed.[6]

A considerable stabilization of "homoleptic" organometallic compounds of the rare earths could be achieved by use of bulky alkyl or aryl groups, such as *tert*-butyl,[7] 2,6-dimethylphenyl,[8] neopentyl,[9] $CH_2Si(CH_3)_3$,[9–11] or $CH[Si(CH_3)_3]_2$,[10] or alkyl and aryl ligands containing built-in chelating groups, like (dimethylamino)-*o*-benzyl or (dimethylamino)methylphenyl.[12,13]

We have found that permethylated complexes of the rare earths can be synthesized by using tetramethylethylenediamine (tmed) as a stabilizing base.[14] We have undertaken single-crystal X-ray diffraction studies of two of these derivatives.[15] Infrared and ^{1}H and ^{13}C NMR spectra of the compounds have been recorded, and some interesting features are presented.

Experimental Section

All reactions and preparations were performed by using Schlenk tubes in an atmosphere of dried, oxygen-free argon. The solvents used were dried and freed of oxygen by refluxing and keeping over NaH or potassium and distillation under argon prior to use. Anhydrous rare-earth chlorides were prepared from the pure

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